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Preparation and Structure of Li-Stabilized Na+ ß" Alumina Single Crystals

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Prepared for Publication

in

Solid State Ionics

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July 1, 1988

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
	Approved for public use and sale;
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	its distribution is unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
Technical Report No. 16	

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Department of Materials Science and Engineering		Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
6532 Boelter Hall University of California, Los Angeles Los Angeles, CA 90024-1595	800 N. Quincy Street Arlington, VA 22217

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
same as #7 above		N00014-83-K-0498

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
Preparation and Structure of Li-Stabilized Na^+ Beta" Alumina Single Crystals

12. PERSONAL AUTHOR(S)
B. Dunn, B. B. Schwarz, J. O. Thomas, and P. E. D. Morgan

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM 8/87 TO 8/88	1988, July 1	

16. SUPPLEMENTARY NOTATION
Submitted to Solid State Ionics

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Li-Stabilized Beta" alumina, crystal growth, crystal structure, X-ray diffraction.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION		
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL	

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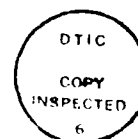S-751 21 Uppsala, Sweden

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ABSTRACT

Single crystals of Li-stabilized Na$^+$ ß" alumina were grown from homogeneous melts of $NaAlO_2$ and $LiVO_3$ on slow cooling from 1600 to 1300°C. Single crystal X-ray diffraction indicates that Li substitutes for Al(2) and Al(4) in an ordered fashion. The Na$^+$ ion distribution exhibits no short-range order effects.

1. INTRODUCTION

The growth of single crystal Na$^+$ ß" alumina is largely limited to two techniques, flux evaporation and skull melting.[1,2] The high temperature crystal pulling methods which were successful with Na ß-alumina are not available for ß" alumina because of the metastability of the ß" phase with respect to the ß phase in the Na_2O-Al_2O_3 binary.[3] The crystal growth of ß" alumina requires the use of Mg, Zn, Co or Ni to stabilize the ß" alumina phase. Although Li is widely employed to stabilize Na$^+$ß" alumina in polycrystalline ceramics, attempts to use Li to stabilize single crystals grown by flux evaporation were unsuccessful.[4] The problem is apparently one of growth temperature (>1600 °C), because the phase study by Hodge clearly demonstrates the stability of the ß" alumina phase at 1500°C.[3] Thus, it would appear that if the melt

temperature could be lowered to ≤1500 °C, it should be possible to grow Li-stabilized $Na^+\beta"$ alumina single crystals. Moreover, the Li-stabilized single crystals would tend to have less problems with intergrowth of $\beta"'$ and $\beta""$ phases, which occurs with Mg-stabilization.[3] In this paper, we report on the use of $NaAlO_2$ and $LiVO_3$ mixed fluxes to grow single crystals of $Na^+ \beta"$ alumina by slow cooling from a homogeneous melt. These single crystals were then analyzed by X-ray diffraction.

2. CRYSTAL GROWTH

A series of compositions were prepared which contained three components; (a) a starting composition close to that of $\beta"$ alumina (called Powder 1), (b) a sodium containing flux and (c) a lithium containing flux. Powder 1 consisted of three component oxides in the ratio of $85Al_2O_3$-$15Na_2O$-$5Li_2O$) (by weight %) mixed by a chemical technique.[5] When this powder was heated slowly to 1600°C in air, it reacted to form pure $\beta"$ alumina. Powder 1 served as the $\beta"$ alumina nutrient in the crystal growth experiments described below.

The sodium and lithium fluxes included Na_2CO_3, $NaAlO_2$, $NaNbO_3$, $LiNbO_3$ and $LiVO_3$. The approach used for preparing the two-component oxides was to mix Li_2CO_3 or Na_2CO_3 with the appropriate oxide and then heat to 2/3 T_m of the respective compounds. The resulting materials were checked for phase purity by X-ray diffraction.

The significant crystal growth experiments are summarized in Table 1. All experiments were performed in air atmosphere using Pt crucibles. The reactants were heated slowly (10 to 12 hours) to the maximum temperature and then cooled for 3 to 5 hours. After heating,

the flux was dissolved in dilute HCl solution so that the product could be analyzed. Although it was possible to obtain ß" alumina using a $LiNbO_3$ flux, $LiVO_3$ was preferred because this flux readily dissolved in dilute HCl. Thus, most composition adjustments were made on systems involving $LiVO_3$ fluxes. Ultimately, it was possible to achieve a phase-pure product of Na^+ ß" alumina. There was no evidence of intergrowth of other aluminate phases, an advantage of the lithium-stabilized system over Mg-stabilized.[3] In addition, there was no indication, either optically or from ESR, that V^{5+} was incorporated in the crystal.

The conditions shown for melt 5 produced thin crystals of Na^+ ß" alumina. In an attempt to grow larger crystals, some seeding and slow-cooling experiments were performed. In these growths, single crystal platelets of Li-stabilized ß" alumina were dispersed randomly in the powders prior to heating. Cooling rates of 6°C/hr and 1°C/hr over the temperature range 1600 to 1300°C were investigated. The lower limit represents the temperature where the last remaining liquid phase was observed. Crystal quality improved significantly with the slower rate and well-defined crystals of the size 3 mm x 3mm x 0.7 mm thick were obtained. In addition to the X-ray diffraction study mentioned below, the crystals were sufficiently large to perform Ag^+ exchange. This experiment provides an approximate method for determining the Na^+ content in ß" alumina and enables one to estimate the crystal composition by assuming that charge balancing arises from substitution of Li^+ for Al^{3+} in the spinel block. For the samples grown at 1°C/hr, the composition was estimated to be $Na_{1.62}Li_{0.31}Al_{10.69}O_{17}$. Unfortunately, the crystals were not sufficiently large to reliably measure ionic conductivity.

3. SINGLE CRYSTAL X-RAY DIFFRACTION STUDY

3.a. Experimental Methods and Refinement

A single crystal of Li-stabilized $Na^+\beta''$ alumina with maximum dimension 0.28 mm and volume 1.1×10^{-3} mm^3 was taken from a large piece. Intensity data were collected on a Nonius CAD4 automatic X-ray diffractometer using graphite monochomatized Mo $K\bar{\alpha}$ radiation and an $\omega/2\theta$ step-scan mode. The methods employed were similar to those used in other β'' alumina structural studies.[6] After first establishing that only reflections of the type *-h+k+l=3n* were present to $2\theta=20°$ (thereby confirming the validity of the $R\bar{3}m$ space group), a total of 2220 reflections of the type *+h,+k, ±l* were collected to $2\theta =100°$. Four reflections were monitored at regular intervals. Each showed a monotonic 7% decrease in intensity during data collection. The measured intensities were corrected accordingly. The measured intensity data were also corrected for background, Lp- factor and absorption effects (μ_{obs}=10.6 cm^{-1}; transmission range : 82-97 %).

The cell parameters were determined from a least-squares refinement of 2θ values measured on the diffractometer for 25 pairs of Friedel reflections. The values are:
a=5.6061(9), c=33.7376(30)Å, V=918.3(4)$Å^3$.

The starting parameters in the refinements were taken from the $Na^+\beta''$ alumina structure.[7] The function minimized was described previously.[6] In the present case, k was set empirically to 0.06. Weak reflections with $F^2_{obs} < 2\sigma(F^2_{obs})$ were removed, leaving a total of 1731 for the final refinements. No correction was found to be needed for extinction. Considerable caution was taken in order to arrive at an optimal model which described the two critical features in the structure; the distribution of Na^+ ions in the conduction plane and the

Li^+ ions in the spinel block.

3.b. Results and Discussion

One prior structural study was reported for Li-stabilized Na^+ β'' alumina.[8] That work utilized neutron powder diffraction and Rietveld refinement techniques since single crystals were not available. The higher intrinsic accuracy of single crystal data, combined with the large difference in the X-ray form factor curves for Li^+ and Al^{3+} make it feasible to obtain a detailed characterization of the Li^+ substitution.

No evidence could be found to suggest any significant level of short-range order in the Na^+ distribution. The arrangement was found to be best described by an anisotropic (β_{ij}) split-atom model using 18h-sites rather than a third-rank vibrational tensor (γ_{ijk}) for axial (6c-site) Na^+ ions. Final positional coordinates and site occupations are listed in Table 2. The refined anisotropic vibrational parameters *can be obtained from one of the authors (JOT)*. Summing the site occupancies, the refined formula unit for the composition is $Na_{1.61(1)}Li_{0.34(2)}Al_{10.66(2)}O_{17}$. No charge neutrality constraint was imposed on the final refinement. This formula unit is in excellent agreement with Ag^+ exchange experiments. It is seen from Fig. 1 that the form of the Na^+ distribution is highly irregular and extended along the directions of the conduction pathways, but with minimal occupation of mid-oxygen (9d) sites. This arrangement explains the difficulties experienced in describing the Na^+ distribution, as well as the relatively poor agreement factors obtained (R(F)≈6%). It is interesting to note that this Na^+ distribution resembles the higher temperature distributions reported for Mg-stabilized Na^+ β'' alumina.[9]

The Li^+ distribution in the spinel block was examined by lowering the symmetry from centrosymmetric $R\bar{3}m$ to non-centrosymmetric

R3m, in turn, for each of the Al sites, and then refining each of the corresponding occupations. This procedure is designed to facilitate the detection of Li^+ substitution on Al sites and the presence of Li-ordering. There was evidence of local ordering similar to that observed previously in the neutron diffraction studies of Mg-stabilized $Na^+\beta"$ alumina(9,10). Here, 85% of the Li^+ ions were found to lie in Al(2) sites; the remainder in Al(4) sites. There is ordering in the Li^+ arrangement such that only alternate Al(2) and Al(4) sites are occupied by Li^+ ions. Moreover, these alternating Li-substituted Al(2) and Al(4) sites occur pairwise, that is, directly above one another in the spinel block. It should be noted, however, that any influence which Li-ordering has on the potential experienced by Na^+ ions in the conduction plane, is apparently not transmitted to the local Na^+ arrangement. The absence of short-range order effects is consistent with the high room temperature ionic mobility expected in the material and observed in polycrystalline samples of the same nominal composition.

Some of the important Li/Al-O and Na-O distances are given in Table 3. Since both Al(2)' and Al(4)' are constrained to maintain their centrosymmetric relationship to Al(2) and Al(4), the differences expected for Li-O and Al-O distances cannot be observed. One interesting comparison is that the mean Li/Al(2)-O distance (1.825Å) is significantly shorter than the corresponding Mg/Al(2)-O distance (1.853Å) in Mg-stabilized $Na^+\beta"$ alumina.[10]

4. CONCLUSIONS

The use of a mixed $NaAlO_2$ and $LiVO_3$ flux enables one to grow single crystals of Li-stabilized $Na^+\beta"$ alumina by slow cooling from a melt. The flux plays the dual role of forming a homogeneous melt at

reduced temperatures and supplying a source of Li for stablilizing the ß" alumina phase. The availability of a homogeneous melt suggests that it should be possible to seed the melt and permit crystal pulling techniques to be realized. At the present time, however, the crystals obtained are too small to perform accurate conductivity measurements. The structure of the Li-stabilized single crystals indicates that Li^+ substitutes for Al(2) and Al(4) in an ordered fashion. There is, however, no indication that the Na^+ ion distribution develops short-range order effects.

ACKNOWLEDGEMENTS

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TABLE 1

Summary of Crystal Growth Experiments

No.	COMPOSITION/RATIO	MAX. TEMP. (°C)	PHASES/COMMENTS
2	Powder 1 + $NaNbO_3$ (1:1)	1500	ß-alumina; sintered only
3	Powder 1 + $LiNbO_3$ + Na_2CO_3 (2:2:1)	1500	ß" alumina + $NaNbO_3$ + small amounts of ß-alumina and $Li_3Nb_3O_8$; melt formed
4	Powder 1 + $NaAlO_2$ + $LiVO_3$ (2:1:1)	1500	ß" alumina with a few extra peaks; melt formed
5	Powder 1 + $NaAlO_2$ + $LiVO_3$ (2:2:1)	1600	ß" alumina only; melt formed

TABLE 2

Refined Fractional Coordinates and Occupancies (expressed as No. atoms/formula unit)

for Li-Stabilized $Na^+\beta''$ Alumina

ATOM	SITE*	OCCUPANCY	x	y	z
Na	18h	1.610(8)	0.1049(22)	x/2	0.1711(1)
Al(1)	3a	1.0	0	0	0
Al(2)	6c	0.967(5) Al +0.033(5) Li	0	0	0.35024(3)
Al(2)'	6c	0.743(5) Al +0.257(5) Li	0	0	-0.35024(3)
Al(3)	18h	6.0	0.33617(9)	x/2	0.07053(1)
Al(4)	6c	1.0 Al	0	0	0.44981(2)
Al(4)'	6c	0.951(13) Al +0.049(13) Li	0	0	-0.44981(2)
O(1)	18h	6.0	0.15530(11)	2x	0.03405(3)
O(2)	6c	2.0	0	0	0.29591(6)
O(3)	6c	2.0	0	0	0.09636(5)
O(4)	18h	6.0	0.16352(10)	2x	0.23559(3)
O(5)	3b	1.0	1/3	2/3	1/6

* $R\bar{3}m$ notation

The figures given in parentheses are standard deviations on the least significant digit

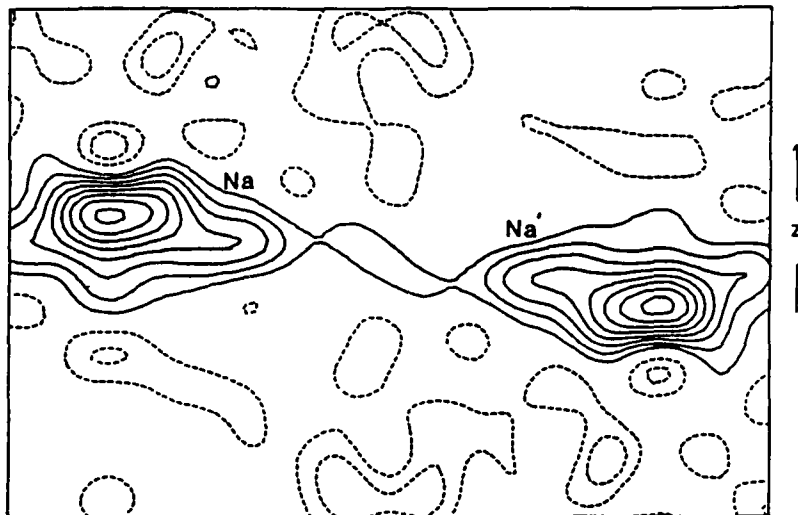# TABLE 3

Some Interatomic Distances in Li-Stabilized Na$^+$ ß" Alumina

		DISTANCE (in Å)	MEAN (in Å)
---			
* Na-Na	(x2)	0.882(16)	
**Na-Na	(x1)	2.238(22)	
Na-O(3)	(x1)	2.571(5)	
Na-O(4)	(x2)	2.591(4)	
Al(1)-O(1)	(x6)	1.896(1)	1.896
Li/Al(2)-O(1)	(x3)	1.823(1)	1.825
-O(2)	(x1)	1.833(2)	
Al(3)-O(1)	(x2)	1.998(1)	1.914
-O(2)	(x1)	1.955(1)	
-O(3)	(x1)	1.850(1)	
-O(4)	(x2)	1.841(1)	
Li/Al(4)-O(5)	(x1)	1.693(1)	1.748
-O(4)	(x3)	1.766(1)	

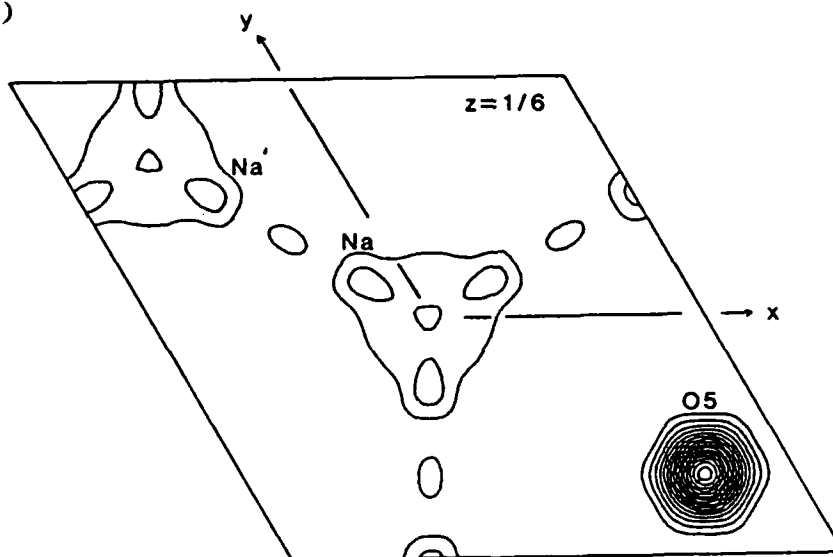
* Between split-atom components

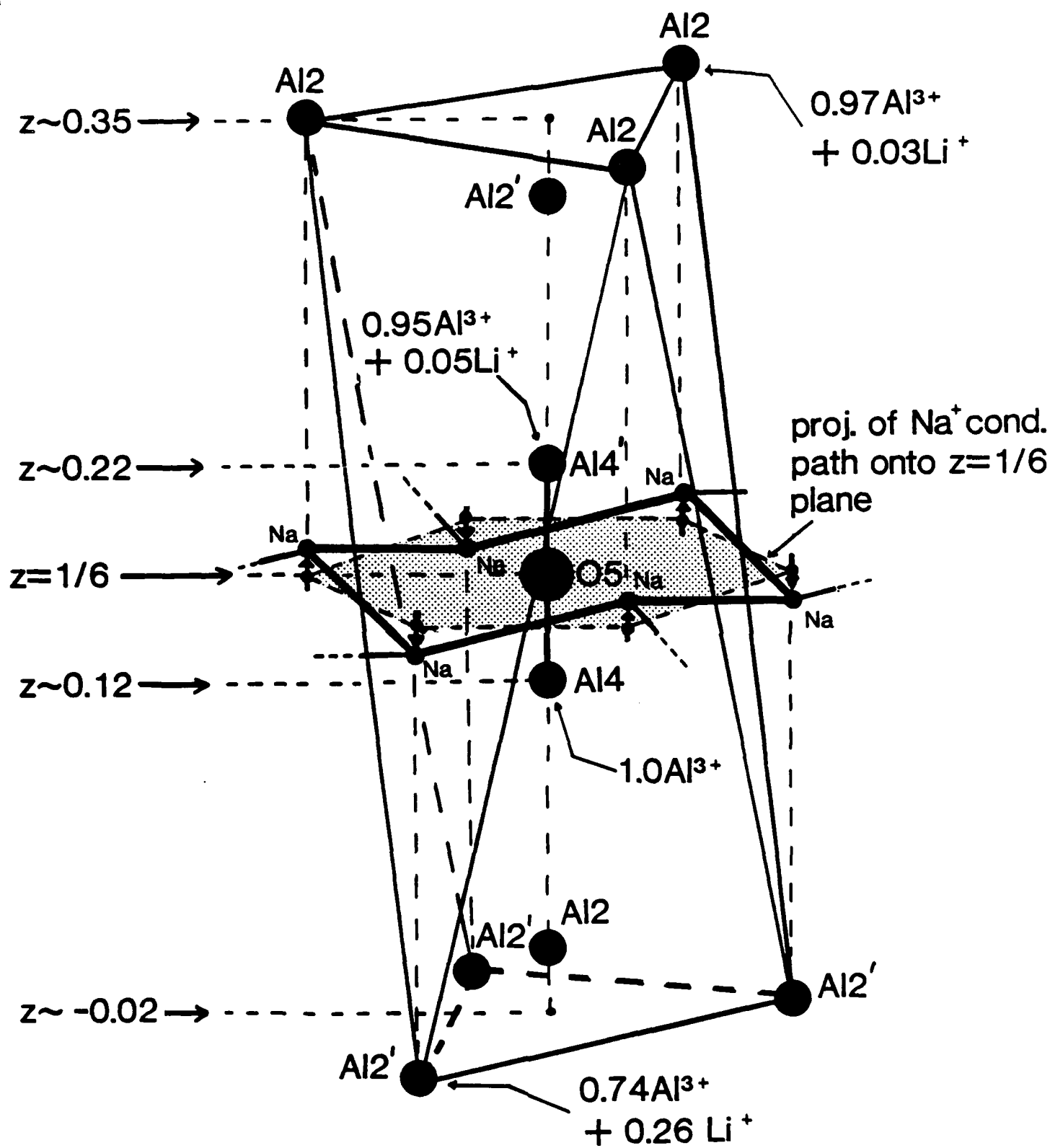** To nearest split-atom component along conduction pathway

FIGURE CAPTION

FIGURE 1. The observed electron density in Li-stabilized Na^+ ß" alumina in
(a) the vertical plane through the Na-Na conduction pathway
(interval: 1.0 e/$Å^3$), and (b) the horizontal z=1/6 conduction plane
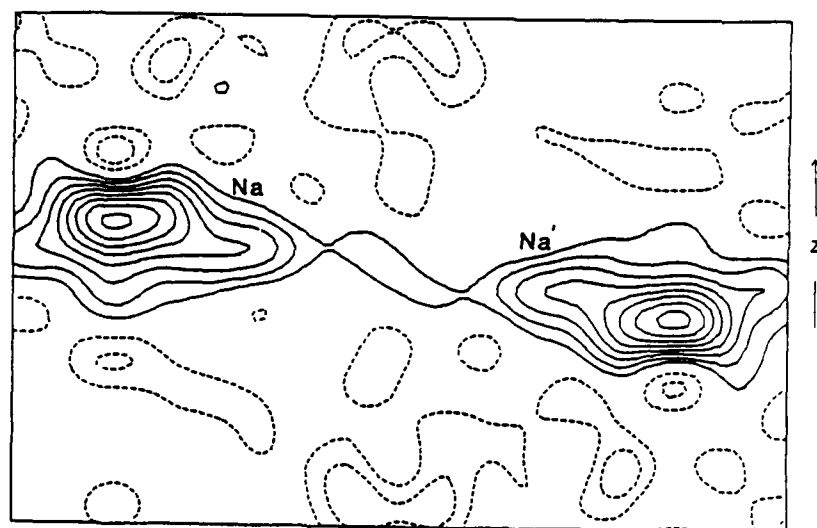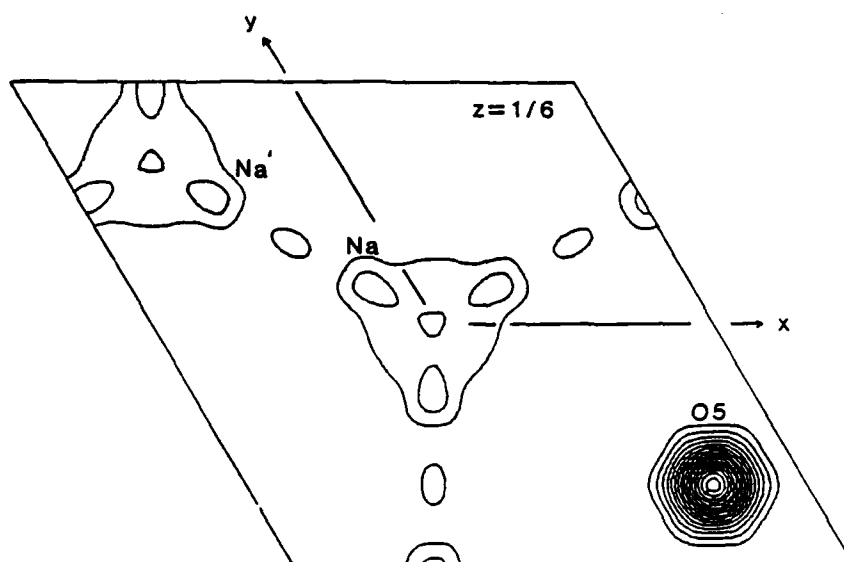(interval: 1.5 e/Å3). The zero contour in not plotted.

(a)

(b)

Al2

z~0.35 →

Al2

Al2

Al2'

0.97Al³⁺
+ 0.03Li⁺

0.95Al³⁺
+ 0.05Li⁺

z~0.22 →

Al4'

Na

proj. of Na⁺cond.
path onto z=1/6
plane

Na

z=1/6 →

Na

O5

Na

Na

z~0.12 →

Al4

Na

1.0Al³⁺

Al2'

Al2

z~ -0.02 →

Al2'

Al2'

0.74Al³⁺
+ 0.26 Li⁺

(a)

(b)

z = 1/6

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